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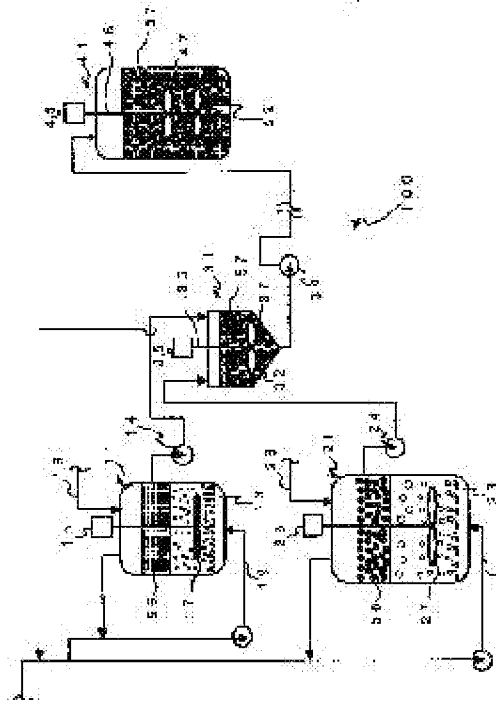
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(54) PROCESS AND APPARATUS FOR PRODUCING GAS HYDRATE



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a process for producing a high concentration gas hydrate which excels in utility in transportation and storage and an apparatus therefor.

SOLUTION: The gas hydrate production apparatus 100 for reacting water with a raw material gas at a specified temperature under a specified pressure to produce a gas hydrate has a first formation tank 11 equipped with a perforated plate 13 for introducing the raw material gas as bubbles into the water, a second formation tank 21 equipped with a perforated plate 23 for introducing bubbles having a diameter greater than the diameter of the pores of the perforated plate 13 in the first forming vessel, and a mixing tank 31 which mixes a fine particulate gas hydrate 55 formed in the first formation tank with a coarse particulate gas hydrate 56 formed in the second formation tank, and produces a mixture 57 of gas hydrates having different particle diameters.

* NOTICES *

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CLAIMS

[Claim(s)]

[Claim 1]While being a manufacturing method of gas-hydrate which makes water and material gas react under specified pressure and prescribed temperature and within a generation tub, and manufactures gas-hydrate and introducing material gas into water in said generation tub as air bubbles, A manufacturing method of gas-hydrate making gas-hydrate of two or more different particle diameter by controlling these air bubbles to two or more different cell diameters generate, and mixing uniformly gas-hydrate of particle diameter of these two or more different

[Claim 2]A manufacturing installation of gas-hydrate characterized by comprising the following.
One or two generation tubs or more which make water and material gas react and manufacture gas-hydrate under specified pressure and prescribed temperature

A mixing means which mixes uniformly gas-hydrate of two or more different particle diameter which introduces material gas into water in said generation tub, and is generated, respectively from air bubbles of an aeration means which generates air bubbles of two or more different paths, and a different diameter beyond 2 ** of this.

[Claim 3]A gas-hydrate manufacturing installation arranging an aeration means from which a cell diameter which two or more generation tubs are made to generate differs in claim 2, respectively.

[Claim 4]A gas-hydrate manufacturing installation characterized by said aeration means being the perforated plate formed in said generation tub lower part in claim 2 or 3.

[Claim 5]A manufacturing installation of gas-hydrate which makes water and material gas react under specified pressure and prescribed temperature characterized by comprising the following, and within a generation tub, and manufactures gas-hydrate.

The 1st generation tub provided with an aeration means which introduces material gas into water as air bubbles of a prescribed diameter.

A mixing means for mixing gas-hydrate from which particle diameter generated, respectively by the 2nd generation tub and said generation tub provided with an aeration means which introduces air bubbles with a bigger path than an aeration means in said 1st generation tub differs.

[Claim 6]A gas-hydrate manufacturing installation provided with the 3rd generation tub provided with an aeration means which introduces air bubbles with a bigger path than an aeration means in said 2nd generation tub.

[Claim 7]A gas-hydrate manufacturing installation characterized by said aeration means being the perforated plate formed in said generation tub lower part in claim 5 or 6.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the method of manufacturing gas-hydrate from natural gas, methane, carbon dioxide, etc. in details more, for example, and the device for it about the manufacturing method and manufacturing installation of gas-hydrate.

[0002]

[Description of the Prior Art]Gas-hydrate is solid matter of the shape of ice which consists of a water molecule and a gas molecule.

It is a hydrate of the structure which incorporated the gas molecule into the inside of the cage structure formed of a water molecule.

Since this gas-hydrate has character, such as generating of the high pressure by high gas concealment nature, big generation and heat of dissociation, and a small temperature change, and the selectivity of hydrate-ized gas, For example, use for various uses, such as transportation and storage means, such as natural gas, and separate recovery of a thermal storage system, an actuator, and gas, attracts attention.

Research is done.

[0003]Although transportation of this gas-hydrate and storage are performed with the gestalt of bulk (powdered) or a slurry, Since the particle diameter of gas-hydrate being dramatically small and particle diameter were comparatively uniform, the volume concentration for in the case of bulk, securing mobility, when pack density becomes small and is a slurry became about 0.15 or less, and there was a problem that the efficiency of transportation or storage was very low.

[0004]For this reason, in JP,2000-302702,A. Supply material gas, water, etc. to the 1st pressure vessel, carry out high speed stirring, and the micro crystallite of methane hydrate is made to generate, Material gas, water, etc. are supplied to the 2nd pressure vessel, it stirs by late agitating speed, a methane hydrate crystal with large particle diameter is deposited, and the invention of the manufacturing method of the gas-hydrate which subsequently mixes both is indicated. Although it is the outstanding method which the art of this JP,2000-302702,A manufactures two sorts of gas-hydrates from which particle diameter differs, is mixed, and provides the suitable gas-hydrate for transportation etc., Since it is what controls particle diameter by agitating speed, at least two or more pressure vessels which need suitable power especially for high speed stirring, and serve as a generation tub are needed.

[0005]

[Problem(s) to be Solved by the Invention]An object of this invention is to provide the method of manufacturing the high-concentration gas-hydrate excellent in the convenience in the case of transportation or storage, and the device for it.

[0006]

[Means for Solving the Problem]In order to solve an aforementioned problem, an invention of a manufacturing method of the gas-hydrate according to claim 1, While being a manufacturing method of gas-hydrate which makes water and material gas react under specified pressure and prescribed temperature and within a generation tub, and manufactures gas-hydrate and introducing material gas into water in said generation tub as air bubbles, Gas-hydrate of two or more different particle diameter by controlling these air bubbles in two or more different paths is made to generate, and gas-hydrate of particle diameter of these two or more different **** is mixed uniformly. While being able to make gas-hydrate of particle diameter which is different by a simple mechanism by controlling a cell diameter of material gas introduced underwater generate easily according to this feature, By mixing uniformly gas-hydrate from which particle diameter differs, high-density gas-hydrate suitable for transportation or storage can be manufactured.

[0007]An invention of the gas-hydrate manufacturing installation according to claim 2 is provided with the following.

One or two generation tubs or more which make water and material gas react and manufacture gas-hydrate under specified pressure and prescribed temperature

5 An aeration means which introduces material gas into water in said generation tub, and makes it generate air bubbles of two or more different paths.

A mixing means which mixes uniformly gas-hydrate of two or more different particle diameter generated from air bubbles of a path of these two or more different ****, respectively.

10 Since it is what is made to generate gas-hydrate from which particle diameter differs by two or more aeration means from which a cell diameter generated, respectively differs, and is mixed according to this feature, high-density gas-hydrate which was suitable for transportation or storage by a comparatively simple equipment configuration can be manufactured efficiently.

[0008]An invention of the gas-hydrate manufacturing installation according to claim 3 arranged
15 an aeration means from which a cell diameter which two or more generation tubs are made to generate differs in claim 2, respectively. According to this feature, since an aeration means from which a cell diameter to generate differs was arranged independently, it is possible to two or more generation tubs to mix, after making gas-hydrate of separate particle diameter generate for every generation tub, and the mixture ratio etc. of gas-hydrate from which particle diameter
20 differs can be easily adjusted to them.

[0009]An invention of the gas-hydrate manufacturing installation according to claim 4 is characterized by said aeration means being the perforated plate formed in said generation tub lower part in claim 2 or 3. According to this feature, gas-hydrate particle diameter is efficiently
25 controllable by a simple mechanism by having formed a perforated plate in the generation tub lower part as an aeration means.

[0010]An invention of the gas-hydrate manufacturing installation according to claim 5 is provided with the following.

30 The 1st generation tub provided with an aeration means which is a manufacturing installation of gas-hydrate which makes water and material gas react under specified pressure and prescribed temperature and within a generation tub, and manufactures gas-hydrate, and introduces material gas into water as air bubbles of a prescribed diameter.

35 The 2nd generation tub provided with an aeration means which introduces air bubbles with a bigger path than an aeration means in said 1st generation tub.

A mixing means for mixing gas-hydrate from which particle diameter generated by said generation tub, respectively differs.

40 According to this feature, a gas-hydrate mixture in which size particle diameter, such as a fine grain and coarse grain, differs, for example can be efficiently manufactured by having composition provided with the 1st generation tub, the 2nd generation tub, and a mixing means.

[0011]An invention of the gas-hydrate manufacturing installation according to claim 6 was provided with the 3rd generation tub provided with an aeration means which introduces air bubbles whose path is still bigger than an aeration means in said 2nd generation tub. According
45 to this feature, three sorts of gas-hydrate mixtures in which particle diameter of a fine grain, an inside grain, coarse grain, etc. differs, for example can be efficiently manufactured by having

composition provided with the 3rd [further] generation tub.

[0012]An invention of the gas-hydrate manufacturing installation according to claim 7 is characterized by said aeration means being the perforated plate formed in said generation tub lower part in claim 5 or 6. According to this feature, gas-hydrate particle diameter is efficiently controllable by a simple mechanism by having formed a perforated plate in the generation tub lower part as an aeration means.

[0013]

[Embodiment of the Invention]A pressure predetermined in the kind of material gas used for manufacture of gas-hydrate by this invention method, Especially if gas-hydrate is formed by temperature conditions, it will not be limited, for example, methane, natural gas (mixed gas, such as methane, ethane, propane, and butane), carbon dioxide (carbon dioxide), etc. can be mentioned. The above-mentioned material gas is underwater introduced as air bubbles, and gas-hydrate is made to generate under specified pressure and prescribed temperature in this invention. Here, although a pressure and temperature conditions required for gas-hydrate generation change with kinds of gas, all can be carried out on condition of known.

[0014]The gas-hydrate of different particle diameter is made to generate in the gas-hydrate manufacturing method of this invention by controlling the cell diameter (size of air bubbles) of the material gas introduced underwater. If a cell diameter is the method of carrying out aeration, for example via a perforated plate or an aeration pipe, it can be adjusted with the size of a hole. By controlling a cell diameter, the reason it becomes possible to make the gas-hydrate of different particle diameter generate is as follows.

[0015]Generally, the gas which contacted water under the predetermined condition is hydrated after dissolving in water, and it generates gas-hydrate. It is thought that in the case of the air bubbles introduced underwater it dissolves in water by a contact surface (namely, cellular surface) with water, and a fixed gas dissolved field is formed in the circumference of air bubbles. Since the dissolved field 53 of the circumference of air bubbles also becomes large at [drawing 3 (a)] when the path of the air bubbles 51 is large as shown in drawing 3, a gas-hydrate generation reaction will be comparatively wide range, and it will go on simultaneously. On the other hand, when the path of the air bubbles 51 is small, since the dissolved field 53 of the circumference of air bubbles becomes small, it becomes what also has a small range in which a gas-hydrate generation reaction advances at [drawing 3 (b)]. Since the air bubbles 51 go up underwater with lift, since gas-hydrate generation is performed over the whole dissolved field for a short time, around the air bubbles of a major diameter with a big dissolved field, gas-hydrate with big particle diameter generates here, but. In the circumference of the air bubbles of a byway, since the gas dissolved field is small, gas-hydrate with small particle diameter will generate. Thus, the particle diameter of the gas-hydrate to generate is controlled by the manufacturing method of this invention using the difference in the dissolved field by the size of a cell diameter. Therefore, for example, if the path of air bubbles is adjusted to smallness into size, the particle diameter of gas-hydrate is also controllable to a major diameter, the diameter of inside, and a byway, respectively. What is necessary is here, for control of perfect particle diameter to be impossible in manufacture of gas-hydrate, and just to be able to distinguish the differences of the above-mentioned particle diameter also including the thing of particle diameter other than the specified

particle size impossibly generated by a manufacturing process by the comparison on the basis of mean particle diameter, since the particle size distribution of a fixed range is taken.

[0016]As an example in the case of considering it as a mixture combining the gas-hydrate of different particle diameter, It is preferred that controlling the average radius of the fine grain at the time of making the average radius of coarse grain into R_L to $0.4R_L - 0.6R_L$ is mentioned, and it makes R_S (average radius of fine grain)/ R_L (average radius of coarse grain) 0.52 to about 0.53 especially. By making the ratio of the particle diameter of coarse grain and a fine grain into the above-mentioned range, the useless opening between the gas-hydrate particles at the time of considering it as a mixture can be made into the minimum, and a high-density mixture is obtained. In about 80 to 90 % of the weight of coarse grain, the mixture ratio of the coarse grain in this case and a fine grain is about 10 to 20 % of the weight of fine grains, is 86 to 88 % of the weight of coarse grain preferably, and is 12 to 14 % of the weight of fine grains, for example. By making the compounding ratio of coarse grain and a fine grain into the above-mentioned range under said particle size ratio, the effect of particle diameter control is fully demonstrated and densification of the gas-hydrate can be carried out.

[0017]The mixture which mixed uniformly the gas-hydrate from which the particle diameter which consists of coarse grain, an inside grain, and a fine grain substantially as an example of another combination differed can be mentioned. In this mixture, controlling the average radius of $0.4R_L - 0.6R_L$, and a fine grain to $0.2R_L - 0.3R_L$ is mentioned in the average radius of the inside grain at the time of making the average radius of coarse grain into R_L . It is preferred to make 0.41 to about 0.42 and R_S (average radius of fine grain)/ R_L (average radius of coarse grain) about into 0.22 to 0.23 for R_M (average radius of inside grain)/ R_L (average radius of coarse grain) especially. By making the ratio of the mean particle diameter of coarse grain, an inside grain, and a fine grain into the above-mentioned range, the useless opening between the gas-hydrate particles at the time of considering it as a mixture can be made into the minimum, and a high-density mixture is obtained. The mixture ratio of the coarse grain in this case, an inside grain, and a fine grain can be used as about 90 to 94 % of the weight of coarse grain, about 5 to 8 % of the weight of inside grains, and about 1 to 2 % of the weight of fine grains, and is 92 to 93 % of the weight of coarse grain, 6 to 7 % of the weight of inside grains, and 1 to 2 % of the weight of fine grains preferably. By making the compounding ratio of coarse grain, an inside grain, and a fine grain into the above-mentioned range under said particle size ratio, the effect of said particle diameter control is fully demonstrated, and densification of the gas-hydrate can be carried out.

[0018]As mentioned above, in addition to the particle diameter of gas-hydrate, in this invention, it becomes possible by controlling the rate of a compounding ratio to attain densification more.

[0019]In this invention, the gas-hydrate from which particle diameter differs, for example, coarse grain and a fine grain, coarse grain, an inside grain, and a fine grain are mixed by homogeneity over the whole, for example by mixing means, such as stirring. Thus, by mixing uniformly, a mixture carries out densification so that the gas-hydrate of an inside grain or a fine grain may fill the gap of coarse-grain gas-hydrates.

[0020]The gestalt of the gas-hydrate mixture of this invention can be made into a bulk state, a slurry regime, etc., for example. If it is in a bulk state, it will become possible by filling up the

gap of coarse grain with a fine grain or an inside grain to carry out the filling factor to the tank conventionally made into about 40 % of the weight to 60% of the weight or more. When it is considered as a slurry regime, in addition to about 15 % of the weight being able to raise conventionally the volume concentration which has been made into a limit and which can be
5 flowed to 30 % of the weight or more, it becomes the gas-hydrate mixed slurry which maintained required mobility.

[0021]Drawing 1 is the gas-hydrate manufacturing installation 100 suitable for manufacture of the gas-hydrate mixture by this invention manufacturing method, and is provided with the fine
10 grain generation tub 11, the coarse-grain generation tub 21, the mixing chamber 31, and the gas-hydrate tank 41 as main composition.

[0022]The fine grain generation tub 11 is provided with cooling methods (not shown), such as a heat exchanger, and it is constituted by the resisting pressure container designed adjust an inside
15 to a predetermined temperature and pressure, The perforated plate 13 which has fine pores in the lower part in a tub is arranged, and the agitator 17 as a mixing means which stirs the liquid phase is formed in the central part. As for the agitator 17, it is preferred to install, when making uniform heat distribution of fine grain generation tub 11 inside and enabling it for a heat
20 exchanger to remove gas-hydrate heat of formation efficiently.

[0023]While supplying gas in a tub from the gas supplying pipelines 19, aeration is made to carry out underwater to the water which was introduced in the tub from the water supply piping
18, and was stored with predetermined volume as small air bubbles via the fine pores of the perforated plate 13 by the fine grain generation tub 11 as an example of a method which
25 manufactures the gas-hydrate of the diameter of a fine grain. Small air bubbles contact water, going up with lift, and make the gas-hydrate of the desired diameter of a fine grain generate under specified pressure and temperature. The fine grain gas-hydrate 55 generated on such conditions surfaces in the aqueous-phase upper part in the fine grain generation tub 11.
Conditions, such as a concrete temperature, a pressure, reaction time, the pole diameter and cell
30 diameter of the perforated plate 13, and a gas mass flow, can be set up according to the size of the fine grain made into the purpose.

[0024]The coarse-grain generation tub 21 is provided with cooling methods (not shown), such as a heat exchanger, like said fine grain generation tub 11, It is constituted by the resisting pressure
35 container designed adjust an inside to a predetermined temperature and pressure, the perforated plate 23 which has a bigger aperture than said perforated plate 13 in the lower part in a tub is arranged, and the agitator 27 as a mixing means which stirs the liquid phase is formed in the central part. As for this agitator 27, it may be preferred to install, when making uniform heat distribution of coarse-grain generation tub 21 inside and enabling it for a heat exchanger to
40 remove gas-hydrate heat of formation efficiently, and the same grade as the stirrer 17 in the fine grain generation tub 11 may be sufficient as agitating speed.

[0025]As an example of the method of manufacturing, the gas-hydrate of the diameter of coarse grain in the coarse-grain generation tub 21. While supplying gas in a tub from the gas supplying
45 pipelines 29, aeration is made to carry out underwater to underwater [which was introduced in the tub from the water supply piping 28, and was stored with predetermined volume] as bigger

air bubbles than said small air bubbles via the hole (an aperture is larger than the perforated plate 13) of the perforated plate 23. These larger air bubbles contact water, going up with lift, and make the gas-hydrate of the desired diameter of coarse grain generate under specified pressure and temperature. The coarse-grain gas-hydrate 56 generated on such conditions surfaces in the aqueous-phase upper part in a generation container. Conditions, such as a concrete temperature, a pressure, reaction time, a cell diameter, an aperture of the perforated plate 23, and a gas mass flow, can be set up according to the size of the coarse grain made into the purpose.

[0026]The fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 which were generated are discharged by operation of the extraction pumps 14 and 24, respectively, and are introduced to the mixing chamber 31 with a predetermined ratio. This mixing chamber 31 is provided with the agitator 32 as a mixing means, and uniformly, the fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 are mixed so that fine grain gas-hydrate may fill the gap of coarse-grain gas-hydrates over the whole. When the high-density restoration type gas-hydrate mixture 57 is obtained, it becomes high-density restoration type gas-hydrate in the handling by a bulk state and it slurs by this, it becomes high-concentration gas hydrate slurry.

[0027]the gas-hydrate mixture 57 after mixing and stirring coarse grain and a fine grain in the device of drawing 1 -- the pump 34 -- the tank 41 -- ***** -- it has composition and is stored in the state where it was stabilized in the tank 41. The agitator 42 for maintaining the manufactured gas-hydrate mixture 57 in the uniform state can also be formed in the tank 41 if needed.

[0028]Although the fine grain generation tub 11 and the coarse-grain generation tub 21 considered it as the separate container in the device of drawing 1, when conditions, such as a pressure, allow, it is also possible to have composition which carries out adjacent arranging of the fine grain generation tub 11 and the coarse-grain generation tub 21, for example to an integral-type container via a septum.

[0029]Also in the case of the ternary system of coarse grain, an inside grain, and a fine grain, the high-concentration gas-hydrate mixture 57 can be manufactured by the equipment configuration and method which applied correspondingly above.

[0030]Drawing 2 is a drawing in which the gas-hydrate manufacturing installation 101 concerning a 2nd embodiment of this invention is shown, and is provided with the gas-hydrate mixture generation tub 61 and the gas-hydrate tank 41 as main composition. Here, it became possible by giving the role of the fine grain generation tub 11 in the manufacturing installation of a 1st embodiment, the coarse-grain generation tub 21, and the mixing chamber 31 to the gas-hydrate mixture generation tub 61 remarkable to make an equipment configuration simple.

[0031]The gas-hydrate mixture generation tub 61 is provided with cooling methods (not shown), such as a heat exchanger, It is constituted by the resisting pressure container designed adjust an inside to a predetermined temperature and pressure, It classifies and the perforated plate 23 which has the perforated plate 13 and the bigger aperture as the 2nd aeration means than said perforated plate 13 which have fine pores as the 1st aeration means in the lower part in a tub is arranged so that the section of the generation tub 61 may be occupied with a predetermined area

ratio. The ratio of the area of this perforated plate 13 and the perforated plate 23 can be set up so that the fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 may be generated by a suitable ratio, for example. The agitator 67 as a mixing means which equipped the position equivalent to the lower part of the upper part and the lower part of the liquid phase with stirring wings is formed in the central part of the gas-hydrate mixture generation tub 61. While this agitator 67 makes uniform heat distribution of gas-hydrate mixture generation tub 61 inside and enables it for a heat exchanger to remove gas-hydrate heat of formation efficiently, In the liquid phase upper part, it has a function which stirs the fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 which were generated, and is mixed uniformly.

[0032]As an example of the method of manufacturing, the gas-hydrate mixture 57 in the gas-hydrate mixture generation tub 61. While supplying gas in a tub from the gas supplying pipelines 69, aeration is made to carry out underwater to the water which was introduced in the tub from the water supply piping 68, and was stored with predetermined volume as bigger air bubbles than the rough hole of the perforated plate 23 simultaneously as air bubbles smaller than the fine pores of the perforated plate 13, respectively. Contact water, while small air bubbles go up with lift, and the desired fine grain gas-hydrate 55 is made to generate under specified pressure and temperature, and big air bubbles make the coarse-grain gas-hydrate 56 generate in the similar manner. The fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 which were generated on such conditions are distributed in the aqueous-phase upper part in a generation container, stirring mixing is carried out here, and the uniform gas-hydrate mixture 57 is obtained. Conditions, such as a concrete temperature, a pressure, reaction time, the path and cell diameter of the perforated plates 13 and 23, and a gas mass flow, can be set up according to the size of the fine grain and coarse grain which are made into the purpose. The generated gas-hydrate mixture 57 is discharged out of a tub by operation of the extraction pump 64, and are collected. What is necessary is just to install what has a hole of size, inside, and smallness by a prescribed area ratio as said perforated plate, in manufacturing the gas-hydrate mixture of coarse grain, an inside grain, and a fine grain.

[0033]Thus, by arranging the perforated plates 13 and 23 with which apertures differ in the gas-hydrate mixture generation tub 61 in a 2nd embodiment, While being able to make the fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 able to generate by a desired ratio simultaneously and being able to collect as a mixture, an equipment configuration can be simplified remarkably. Since other composition in a 2nd embodiment is the same as that of a 1st embodiment, it gives the same numerals to the same composition, and omits explanation.

[0034]

[Example]Next, although an example etc. are given and this invention is explained in more detail, this invention is not restrained at all by this.

[0035]By the gas-hydrate manufacturing installation of composition of being shown in example 1 drawing 1, natural gas and water were used as the raw material, and the natural gas-hydrate mixture was manufactured.

[0036]In manufacture of coarse grain, by adjusting temperature, a pressure, and a cell diameter, it controlled so that an average radius was set to about 0.5 mm. Similarly, in manufacture of a

fine grain, it controlled so that an average radius was set to about 0.25 mm. The ratio (R_S/R_L) of the average radius of coarse grain and a fine grain was about 0.5.

[0037]By mixing the coarse grain and the fine grain of natural gas-hydrate which were obtained with the mixture ratio of 85:15, this invention natural gas-hydrate mixed slurry was manufactured. Pack density [in / in this gas-hydrate mixture / a storage kettle] was 30%.

[0038]It was considered as the comparative example 1 by the natural gas-hydrate of the coarse grain manufactured in comparative example 1 Example 1. Pack density [in / in this natural gas-hydrate / a storage kettle] was 20 to 25%.

[0039]It was considered as the comparative example 2 by the natural gas-hydrate of the fine grain manufactured in comparative example 2 Example 1. Pack density [in / in this natural gas-hydrate / a storage kettle] was 10 to 15%.

[0040]

[Effect of the Invention]According to this invention, a gas-hydrate mixture convenient for transportation or storage can be easily manufactured by a simple equipment configuration by the high density uniformly mixed with the particle size ratio and the mixture ratio of a request of the gas-hydrate from which a size differs.

TECHNICAL FIELD

[Field of the Invention]This invention relates to the method of manufacturing gas-hydrate from natural gas, methane, carbon dioxide, etc. in details more, for example, and the device for it about the manufacturing method and manufacturing installation of gas-hydrate.

PRIOR ART

[Description of the Prior Art]Gas-hydrate is solid matter of the shape of ice which consists of a water molecule and a gas molecule.

It is a hydrate of the structure which incorporated the gas molecule into the inside of the cage structure formed of a water molecule.

Since this gas-hydrate has character, such as generating of the high pressure by high gas concealment nature, big generation and heat of dissociation, and a small temperature change, and the selectivity of hydrate-ized gas, For example, use for various uses, such as transportation and storage means, such as natural gas, and separate recovery of a thermal storage system, an actuator, and gas, attracts attention.

Research is done.

[0003]Although transportation of this gas-hydrate and storage are performed with the gestalt of bulk (powdered) or a slurry, Since the particle diameter of gas-hydrate being dramatically small and particle diameter were comparatively uniform, the volume concentration for in the case of bulk, securing mobility, when pack density becomes small and is a slurry became about 0.15 or less, and there was a problem that the efficiency of transportation or storage was very low.

[0004]For this reason, in JP,2000-302702,A. Supply material gas, water, etc. to the 1st pressure vessel, carry out high speed stirring, and the micro crystallite of methane hydrate is made to generate, Material gas, water, etc. are supplied to the 2nd pressure vessel, it stirs by late agitating speed, a methane hydrate crystal with large particle diameter is deposited, and the invention of the manufacturing method of the gas-hydrate which subsequently mixes both is indicated. Although it is the outstanding method which the art of this JP,2000-302702,A manufactures two sorts of gas-hydrates from which particle diameter differs, is mixed, and provides the suitable gas-hydrate for transportation etc., Since it is what controls particle diameter by agitating speed, at least two or more pressure vessels which need suitable power especially for high speed stirring, and serve as a generation tub are needed.

EFFECT OF THE INVENTION

[Effect of the Invention]According to this invention, a gas-hydrate mixture convenient for transportation or storage can be easily manufactured by a simple equipment configuration by the high density uniformly mixed with the particle size ratio and the mixture ratio of a request of the gas-hydrate from which a size differs.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]An object of this invention is to provide the method of manufacturing the high-concentration gas-hydrate excellent in the convenience in the case of transportation or storage, and the device for it.

MEANS

[Means for Solving the Problem]In order to solve an aforementioned problem, an invention of a manufacturing method of the gas-hydrate according to claim 1, While being a manufacturing method of gas-hydrate which makes water and material gas react under specified pressure and prescribed temperature and within a generation tub, and manufactures gas-hydrate and introducing material gas into water in said generation tub as air bubbles, Gas-hydrate of two or

more different particle diameter by controlling these air bubbles in two or more different paths is made to generate, and gas-hydrate of particle diameter of these two or more different **** is mixed uniformly. While being able to make gas-hydrate of particle diameter which is different by a simple mechanism by controlling a cell diameter of material gas introduced underwater generate easily according to this feature, By mixing uniformly gas-hydrate from which particle diameter differs, high-density gas-hydrate suitable for transportation or storage can be manufactured.

[0007]An invention of the gas-hydrate manufacturing installation according to claim 2 is provided with the following.

One or two generation tubs or more which make water and material gas react and manufacture gas-hydrate under specified pressure and prescribed temperature

An aeration means which introduces material gas into water in said generation tub, and makes it generate air bubbles of two or more different paths.

A mixing means which mixes uniformly gas-hydrate of two or more different particle diameter generated from air bubbles of a path of these two or more different ****, respectively.

Since it is what is made to generate gas-hydrate from which particle diameter differs by two or more aeration means from which a cell diameter generated, respectively differs, and is mixed according to this feature, high-density gas-hydrate which was suitable for transportation or storage by a comparatively simple equipment configuration can be manufactured efficiently.

[0008]An invention of the gas-hydrate manufacturing installation according to claim 3 arranged an aeration means from which a cell diameter which two or more generation tubs are made to generate differs in claim 2, respectively. According to this feature, since an aeration means from which a cell diameter to generate differs was arranged independently, it is possible to two or more generation tubs to mix, after making gas-hydrate of separate particle diameter generate for every generation tub, and the mixture ratio etc. of gas-hydrate from which particle diameter differs can be easily adjusted to them.

[0009]An invention of the gas-hydrate manufacturing installation according to claim 4 is characterized by said aeration means being the perforated plate formed in said generation tub lower part in claim 2 or 3. According to this feature, gas-hydrate particle diameter is efficiently controllable by a simple mechanism by having formed a perforated plate in the generation tub lower part as an aeration means.

[0010]An invention of the gas-hydrate manufacturing installation according to claim 5 is provided with the following.

The 1st generation tub provided with an aeration means which is a manufacturing installation of gas-hydrate which makes water and material gas react under specified pressure and prescribed temperature and within a generation tub, and manufactures gas-hydrate, and introduces material gas into water as air bubbles of a prescribed diameter.

The 2nd generation tub provided with an aeration means which introduces air bubbles with a bigger path than an aeration means in said 1st generation tub.

A mixing means for mixing gas-hydrate from which particle diameter generated by said generation tub, respectively differs.

According to this feature, a gas-hydrate mixture in which size particle diameter, such as a fine

grain and coarse grain, differs, for example can be efficiently manufactured by having composition provided with the 1st generation tub, the 2nd generation tub, and a mixing means.

[0011]An invention of the gas-hydrate manufacturing installation according to claim 6 was provided with the 3rd generation tub provided with an aeration means which introduces air bubbles whose path is still bigger than an aeration means in said 2nd generation tub. According to this feature, three sorts of gas-hydrate mixtures in which particle diameter of a fine grain, an inside grain, coarse grain, etc. differs, for example can be efficiently manufactured by having composition provided with the 3rd [further] generation tub.

[0012]An invention of the gas-hydrate manufacturing installation according to claim 7 is characterized by said aeration means being the perforated plate formed in said generation tub lower part in claim 5 or 6. According to this feature, gas-hydrate particle diameter is efficiently controllable by a simple mechanism by having formed a perforated plate in the generation tub lower part as an aeration means.

[0013]

[Embodiment of the Invention]A pressure predetermined in the kind of material gas used for manufacture of gas-hydrate by this invention method, Especially if gas-hydrate is formed by temperature conditions, it will not be limited, for example, methane, natural gas (mixed gas, such as methane, ethane, propane, and butane), carbon dioxide (carbon dioxide), etc. can be mentioned. The above-mentioned material gas is underwater introduced as air bubbles, and gas-hydrate is made to generate under specified pressure and prescribed temperature in this invention. Here, although a pressure and temperature conditions required for gas-hydrate generation change with kinds of gas, all can be carried out on condition of known.

[0014]The gas-hydrate of different particle diameter is made to generate in the gas-hydrate manufacturing method of this invention by controlling the cell diameter (size of air bubbles) of the material gas introduced underwater. If a cell diameter is the method of carrying out aeration, for example via a perforated plate or an aeration pipe, it can be adjusted with the size of a hole. By controlling a cell diameter, the reason it becomes possible to make the gas-hydrate of different particle diameter generate is as follows.

[0015]Generally, the gas which contacted water under the predetermined condition is hydrated after dissolving in water, and it generates gas-hydrate. It is thought that in the case of the air bubbles introduced underwater it dissolves in water by a contact surface (namely, cellular surface) with water, and a fixed gas dissolved field is formed in the circumference of air bubbles. Since the dissolved field 53 of the circumference of air bubbles also becomes large at [drawing 3 (a)] when the path of the air bubbles 51 is large as shown in drawing 3, a gas-hydrate generation reaction will be comparatively wide range, and it will go on simultaneously. On the other hand, when the path of the air bubbles 51 is small, since the dissolved field 53 of the circumference of air bubbles becomes small, it becomes what also has a small range in which a gas-hydrate generation reaction advances at [drawing 3 (b)]. Since the air bubbles 51 go up underwater with lift, since gas-hydrate generation is performed over the whole dissolved field for a short time, around the air bubbles of a major diameter with a big dissolved field, gas-hydrate with big particle diameter generates here, but. In the circumference of the air bubbles of a byway, since

the gas dissolved field is small, gas-hydrate with small particle diameter will generate. Thus, the particle diameter of the gas-hydrate to generate is controlled by the manufacturing method of this invention using the difference in the dissolved field by the size of a cell diameter. Therefore, for example, if the path of air bubbles is adjusted to smallness into size, the particle diameter of gas-hydrate is also controllable to a major diameter, the diameter of inside, and a byway, respectively. What is necessary is here, for control of perfect particle diameter to be impossible in manufacture of gas-hydrate, and just to be able to distinguish the differences of the above-mentioned particle diameter also including the thing of particle diameter other than the specified particle size impossibly generated by a manufacturing process by the comparison on the basis of mean particle diameter, since the particle size distribution of a fixed range is taken.

[0016]As an example in the case of considering it as a mixture combining the gas-hydrate of different particle diameter, It is preferred that controlling the average radius of the fine grain at the time of making the average radius of coarse grain into R_L to $0.4R_L - 0.6R_L$ is mentioned, and it makes R_S (average radius of fine grain)/ R_L (average radius of coarse grain) 0.52 to about 0.53 especially. By making the ratio of the particle diameter of coarse grain and a fine grain into the above-mentioned range, the useless opening between the gas-hydrate particles at the time of considering it as a mixture can be made into the minimum, and a high-density mixture is obtained. In about 80 to 90 % of the weight of coarse grain, the mixture ratio of the coarse grain in this case and a fine grain is about 10 to 20 % of the weight of fine grains, is 86 to 88 % of the weight of coarse grain preferably, and is 12 to 14 % of the weight of fine grains, for example. By making the compounding ratio of coarse grain and a fine grain into the above-mentioned range under said particle size ratio, the effect of particle diameter control is fully demonstrated and densification of the gas-hydrate can be carried out.

[0017]The mixture which mixed uniformly the gas-hydrate from which the particle diameter which consists of coarse grain, an inside grain, and a fine grain substantially as an example of another combination differed can be mentioned. In this mixture, controlling the average radius of $0.4R_L - 0.6R_L$, and a fine grain to $0.2R_L - 0.3R_L$ is mentioned in the average radius of the inside grain at the time of making the average radius of coarse grain into R_L . It is preferred to make 0.41 to about 0.42 and R_S (average radius of fine grain)/ R_L (average radius of coarse grain) about into 0.22 to 0.23 for R_M (average radius of inside grain)/ R_L (average radius of coarse grain) especially. By making the ratio of the mean particle diameter of coarse grain, an inside grain, and a fine grain into the above-mentioned range, the useless opening between the gas-hydrate particles at the time of considering it as a mixture can be made into the minimum, and a high-density mixture is obtained. The mixture ratio of the coarse grain in this case, an inside grain, and a fine grain can be used as about 90 to 94 % of the weight of coarse grain, about 5 to 8 % of the weight of inside grains, and about 1 to 2 % of the weight of fine grains, and is 92 to 93 % of the weight of coarse grain, 6 to 7 % of the weight of inside grains, and 1 to 2 % of the weight of fine grains preferably. By making the compounding ratio of coarse grain, an inside grain, and a fine grain into the above-mentioned range under said particle size ratio, the effect of said particle diameter control is fully demonstrated, and densification of the gas-hydrate can be carried out.

[0018]As mentioned above, in addition to the particle diameter of gas-hydrate, in this invention, it becomes possible by controlling the rate of a compounding ratio to attain densification more.

[0019]In this invention, the gas-hydrate from which particle diameter differs, for example, coarse grain and a fine grain, coarse grain, an inside grain, and a fine grain are mixed by homogeneity over the whole, for example by mixing means, such as stirring. Thus, by mixing uniformly, a mixture carries out densification so that the gas-hydrate of an inside grain or a fine grain may fill the gap of coarse-grain gas-hydrates.

[0020]The gestalt of the gas-hydrate mixture of this invention can be made into a bulk state, a slurry regime, etc., for example. If it is in a bulk state, it will become possible by filling up the gap of coarse grain with a fine grain or an inside grain to carry out the filling factor to the tank conventionally made into about 40 % of the weight to 60% of the weight or more. When it is considered as a slurry regime, in addition to about 15 % of the weight being able to raise conventionally the volume concentration which has been made into a limit and which can be flowed to 30 % of the weight or more, it becomes the gas-hydrate mixed slurry which maintained required mobility.

[0021]Drawing 1 is the gas-hydrate manufacturing installation 100 suitable for manufacture of the gas-hydrate mixture by this invention manufacturing method, and is provided with the fine grain generation tub 11, the coarse-grain generation tub 21, the mixing chamber 31, and the gas-hydrate tank 41 as main composition.

[0022]The fine grain generation tub 11 is provided with cooling methods (not shown), such as a heat exchanger, and it is constituted by the resisting pressure container designed adjust an inside to a predetermined temperature and pressure, The perforated plate 13 which has fine pores in the lower part in a tub is arranged, and the agitator 17 as a mixing means which stirs the liquid phase is formed in the central part. As for the agitator 17, it is preferred to install, when making uniform heat distribution of fine grain generation tub 11 inside and enabling it for a heat exchanger to remove gas-hydrate heat of formation efficiently.

[0023]While supplying gas in a tub from the gas supplying pipelines 19, aeration is made to carry out underwater to the water which was introduced in the tub from the water supply piping 18, and was stored with predetermined volume as small air bubbles via the fine pores of the perforated plate 13 by the fine grain generation tub 11 as an example of a method which manufactures the gas-hydrate of the diameter of a fine grain. Small air bubbles contact water, going up with lift, and make the gas-hydrate of the desired diameter of a fine grain generate under specified pressure and temperature. The fine grain gas-hydrate generated on such conditions surfaces in the aqueous-phase upper part in the fine grain generation tub 11. Conditions, such as a concrete temperature, a pressure, reaction time, the pole diameter and cell diameter of the perforated plate 13, and a gas mass flow, can be set up according to the size of the fine grain made into the purpose.

[0024]The coarse-grain generation tub 21 is provided with cooling methods (not shown), such as a heat exchanger, like said fine grain generation tub 11, It is constituted by the resisting pressure container designed adjust an inside to a predetermined temperature and pressure, the perforated plate 23 which has a bigger aperture than said perforated plate 13 in the lower part in a tub is arranged, and the agitator 27 as a mixing means which stirs the liquid phase is formed in the central part. As for this agitator 27, it may be preferred to install, when making uniform heat

distribution of coarse-grain generation tub 21 inside and enabling it for a heat exchanger to remove gas-hydrate heat of formation efficiently, and the same grade as the stirrer 17 in the fine grain generation tub 11 may be sufficient as agitating speed.

5 [0025]As an example of the method of manufacturing, the gas-hydrate of the diameter of coarse grain in the coarse-grain generation tub 21. While supplying gas in a tub from the gas supplying pipelines 29, aeration is made to carry out underwater to underwater [which was introduced in the tub from the water supply piping 28, and was stored with predetermined volume] as bigger air bubbles than said small air bubbles via the hole (an aperture is larger than the perforated plate 10 13) of the perforated plate 23. These larger air bubbles contact water, going up with lift, and make the gas-hydrate of the desired diameter of coarse grain generate under specified pressure and temperature. The coarse-grain gas-hydrate 56 generated on such conditions surfaces in the aqueous-phase upper part in a generation container. Conditions, such as a concrete temperature, a pressure, reaction time, a cell diameter, an aperture of the perforated plate 23, and a gas mass 15 flow, can be set up according to the size of the coarse grain made into the purpose.

[0026]The fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 which were generated are discharged by operation of the extraction pumps 14 and 24, respectively, and are introduced to the mixing chamber 31 with a predetermined ratio. This mixing chamber 31 is provided with 20 the agitator 32 as a mixing means, and uniformly, the fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 are mixed so that fine grain gas-hydrate may fill the gap of coarse-grain gas-hydrates over the whole. When the high-density restoration type gas-hydrate mixture 57 is obtained, it becomes high-density restoration type gas-hydrate in the handling by a bulk state and it slurs by this, it becomes high-concentration gas hydrate slurry.

25 [0027]the gas-hydrate mixture 57 after mixing and stirring coarse grain and a fine grain in the device of drawing 1 -- the pump 34 -- the tank 41 -- ***** -- it has composition and is stored in the state where it was stabilized in the tank 41. The agitator 42 for maintaining the manufactured gas-hydrate mixture 57 in the uniform state can also be formed in the tank 41 if 30 needed.

[0028]Although the fine grain generation tub 11 and the coarse-grain generation tub 21 considered it as the separate container in the device of drawing 1, when conditions, such as a pressure, allow, it is also possible to have composition which carries out adjacent arranging of 35 the fine grain generation tub 11 and the coarse-grain generation tub 21, for example to an integral-type container via a septum.

[0029]Also in the case of the ternary system of coarse grain, an inside grain, and a fine grain, the high-concentration gas-hydrate mixture 57 can be manufactured by the equipment configuration and method which applied correspondingly above. 40

[0030]Drawing 2 is a drawing in which the gas-hydrate manufacturing installation 101 concerning a 2nd embodiment of this invention is shown, and is provided with the gas-hydrate mixture generation tub 61 and the gas-hydrate tank 41 as main composition. Here, it became 45 possible by giving the role of the fine grain generation tub 11 in the manufacturing installation of a 1st embodiment, the coarse-grain generation tub 21, and the mixing chamber 31 to the gas-

hydrate mixture generation tub 61 remarkable to make an equipment configuration simple.

[0031]The gas-hydrate mixture generation tub 61 is provided with cooling methods (not shown), such as a heat exchanger, It is constituted by the resisting pressure container designed adjust an inside to a predetermined temperature and pressure, It classifies and the perforated plate 23 which has the perforated plate 13 and the bigger aperture as the 2nd aeration means than said perforated plate 13 which have fine pores as the 1st aeration means in the lower part in a tub is arranged so that the section of the generation tub 61 may be occupied with a predetermined area ratio. The ratio of the area of this perforated plate 13 and the perforated plate 23 can be set up so that the fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 may be generated by a suitable ratio, for example. The agitator 67 as a mixing means which equipped the position equivalent to the lower part of the upper part and the lower part of the liquid phase with stirring wings is formed in the central part of the gas-hydrate mixture generation tub 61. While this agitator 67 makes uniform heat distribution of gas-hydrate mixture generation tub 61 inside and enables it for a heat exchanger to remove gas-hydrate heat of formation efficiently, In the liquid phase upper part, it has a function which stirs the fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 which were generated, and is mixed uniformly.

[0032]As an example of the method of manufacturing, the gas-hydrate mixture 57 in the gas-hydrate mixture generation tub 61. While supplying gas in a tub from the gas supplying pipelines 69, aeration is made to carry out underwater to the water which was introduced in the tub from the water supply piping 68, and was stored with predetermined volume as bigger air bubbles than the rough hole of the perforated plate 23 simultaneously as air bubbles smaller than the fine pores of the perforated plate 13, respectively. Contact water, while small air bubbles go up with lift, and the desired fine grain gas-hydrate 55 is made to generate under specified pressure and temperature, and big air bubbles make the coarse-grain gas-hydrate 56 generate in the similar manner. The fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 which were generated on such conditions are distributed in the aqueous-phase upper part in a generation container, stirring mixing is carried out here, and the uniform gas-hydrate mixture 57 is obtained. Conditions, such as a concrete temperature, a pressure, reaction time, the path and cell diameter of the perforated plates 13 and 23, and a gas mass flow, can be set up according to the size of the fine grain and coarse grain which are made into the purpose. The generated gas-hydrate mixture 57 is discharged out of a tub by operation of the extraction pump 64, and are collected. What is necessary is just to install what has a hole of size, inside, and smallness by a prescribed area ratio as said perforated plate, in manufacturing the gas-hydrate mixture of coarse grain, an inside grain, and a fine grain.

[0033]Thus, by arranging the perforated plates 13 and 23 with which apertures differ in the gas-hydrate mixture generation tub 61 in a 2nd embodiment, While being able to make the fine grain gas-hydrate 55 and the coarse-grain gas-hydrate 56 able to generate by a desired ratio simultaneously and being able to collect as a mixture, an equipment configuration can be simplified remarkably. Since other composition in a 2nd embodiment is the same as that of a 1st embodiment, it gives the same numerals to the same composition, and omits explanation.

EXAMPLE

5 [Example]Next, although an example etc. are given and this invention is explained in more detail, this invention is not restrained at all by this.

10 [0035]By the gas-hydrate manufacturing installation of composition of being shown in example 1 drawing 1, natural gas and water were used as the raw material, and the natural gas-hydrate mixture was manufactured.

15 [0036]In manufacture of coarse grain, by adjusting temperature, a pressure, and a cell diameter, it controlled so that an average radius was set to about 0.5 mm. Similarly, in manufacture of a fine grain, it controlled so that an average radius was set to about 0.25 mm. The ratio (R_S/R_L) of the average radius of coarse grain and a fine grain was about 0.5.

20 [0037]By mixing the coarse grain and the fine grain of natural gas-hydrate which were obtained with the mixture ratio of 85:15, this invention natural gas-hydrate mixed slurry was manufactured. Pack density [in / in this gas-hydrate mixture / a storage kettle] was 30%.

[0038]It was considered as the comparative example 1 by the natural gas-hydrate of the coarse grain manufactured in comparative example 1 Example 1. Pack density [in / in this natural gas-hydrate / a storage kettle] was 20 to 25%.

25 [0039]It was considered as the comparative example 2 by the natural gas-hydrate of the fine grain manufactured in comparative example 2 Example 1. Pack density [in / in this natural gas-hydrate / a storage kettle] was 10 to 15%.

30

DESCRIPTION OF DRAWINGS

35 [Brief Description of the Drawings]

[Drawing 1]The drawing with which explanation of a 1st embodiment of this invention gas-hydrate manufacturing installation is presented.

40 [Drawing 2]The drawing with which explanation of a 2nd embodiment of this invention gas-hydrate manufacturing installation is presented.

45 [Drawing 3]It is a mimetic diagram which presents explanation with the state of the air bubbles of underwater material gas, and the state where air bubbles produce (a) and the dissolved field has produced (b) to small air bubbles, respectively is shown.

[Description of Notations]

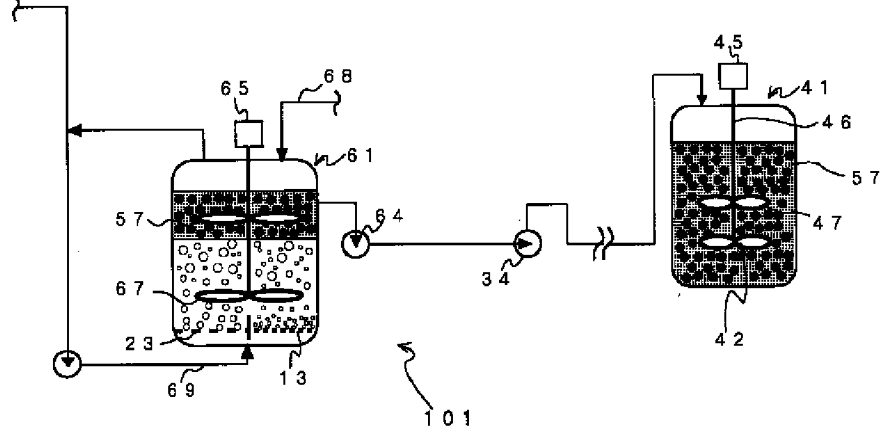
	11 Fine grain generation tub
	14 Extraction pump
	15 Actuator
5	17 Agitator
	18 Water supply piping
	19 Gas supplying pipelines
	21 Coarse-grain generation tub
	23 Perforated plate
10	24 Extraction pump
	25 Actuator
	27 Agitator
	28 Water supply piping
	29 Gas supplying pipelines
15	31 Mixing chamber
	32 Agitator
	34 Extraction pump
	35 Actuator
	36 Stirring shaft
20	37 Stirring wings
	41 Tank
	42 Agitator
	45 Motor
	46 Stirring shaft
25	47 Wings
	51 Air bubbles
	53 Gas dissolved field
	55 Fine grain gas-hydrate
	56 Coarse-grain gas-hydrate
30	57 Gas-hydrate mixture
	61 Gas-hydrate mixture generation tub
	64 Extraction pump
	65 Actuator
	67 Agitator
35	68 Water supply piping
	69 Gas supplying pipelines

40

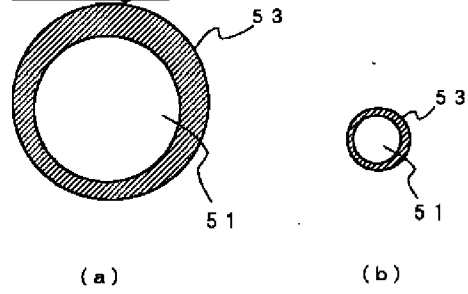
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DRAWINGS

5 [Drawing 2]



[Drawing 3]



10

(a)

(b)

[Drawing 1]

